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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 5 :</b> C08K 11/00, 9/02, A01G 9/22 C03C 14/00		A2	<b>(11) International Publication Number:</b> WO 94/05727 <b>(43) International Publication Date:</b> 17 March 1994 (17.03.94)
<b>(21) International Application Number:</b> PCT/EP93/02380 <b>(22) International Filing Date:</b> 31 August 1993 (31.08.93)		<b>(74) Agent:</b> KUPECZ, Arpád; Octrooibureau Los en Stigter B.V., Weteringschans 96, NL-1017 XS Amsterdam (NL).	
<b>(30) Priority data:</b> 9201568 9 September 1992 (09.09.92) NL P 42 30 023.1 10 September 1992 (10.09.92) DE		<b>(81) Designated States:</b> AU, BR, CA, FI, HU, JP, KR, NZ, RU, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
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<b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> DAPONTE, Tony, Leon, Filip [BE/BE]; Melis Stokelaan 7, B-2050 Antwerp-L.O. (BE). VERSCHAEREN, Patrick, Corneel, Mathilde [BE/BE]; Fresialaan 3, B-2960 Brecht (BE). KIESER, Manfred [DE/DE]; Händelstrasse 39, D-64291 Darmstadt (DE). EDLER, Gerhard [DE/DE]; Königsstätter Strasse 24, D-65468 Trebur (DE).			

**(54) Title:** COMPOSITE MATERIAL FOR THE SCREENING OF RADIATION

**(57) Abstract**

Composite material for the screening of radiation, comprising a polymer, an additive and the customary stabilizers and processing aids necessary for the particular polymer. The additive is preferably an interference pigment.

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WO 94/05727

PCT/EP93/02380

Composite material for the screening of radiation

The present invention relates to a polymeric substance and an additive for the screening of solar radiation with the aim of influencing plant growth and the morphogenesis.

5 It is necessary for a controllable growth of plants to set up special light conditions to affect plant growth and morphogenesis. Special light conditions for plant growth, for example, within a greenhouse or under a mulch film include some which are of particular interest. The temperature within 10 the enclosed area and the light intensity and the spectral distribution of the incoming light are important factors for the plant growth.

Plants, for example, in a greenhouse will grow so well if the variations in temperature between day and night, 15 because of too much sunlight at day and because of too large a decline in temperature at night, are too large since they build a resistance to the variations in temperature. From this it follows that the plants stay back in growth. Thus, for the photosynthesis in greenhouses the photosynthetically 20 active radiation (PAR) is only desired while other parts of the solar light should be screened because they have mainly a negative influence on the microclimate. Therefore the following objectives have to be achieved. Firstly, the intensive irradiation by sunlight in particular by NIR radiation needs 25 to be screened, in order to avoid too high temperatures within the enclosed area. Secondly, the incoming light beams are to be scattered in order to prevent burnings on plants. Thirdly, heat within the area is to be stored at night.

However, in case of mulch films the opposite effect 30 is desired. The PAR should be screened and all other parts of the solar light should be transmitted. Mulch films are used in agriculture to improve the growing conditions of the useful plants and to minimize the use of chemical herbicides.

For certain crop growers want to intervene in the 35 plant morphogenesis. Morphogenesis is the influence from environmental factors on the shape and appearance of the plant. One of them is the light quality. It means that the spectral energy distribution has an effect on the growth of plants.

Raviv and Allingham describe in "Plastic Culture", No. 59, September 1989, pp. 3 to 12, that diffuse light is favourable for a steady growth of plants. Furthermore, it turned out that diffuse light has the advantage that the 5 plants are not going to be damaged. Hancock describes in "Plastic Culture", No. 79, 1988, pp. 4 to 14, that special additives in LDPE have a favourable effect on the microclimate in greenhouses because of the generation of diffuse light and the creation of a favourably thermic effect in the green- 10 houses. Suitable additives are aluminosilicate in the form of kaolin, calcium carbonate, talc and kaolin clay.

Greenhouses made of glass already fulfil some of the above-mentioned conditions by virtue of the inherent physical properties of inorganic glasses. Furthermore, constructive 15 measures, for example knurled glass or shadow cloth are known.

If the enclosing material is plastic, such as, for example, polyethylene, polyethylene/vinyl acetate copolymers, polyvinyl chloride, polycarbonate or polyacrylate, it is much 20 more difficult to meet these requirements. The high transparency of many plastics for IR radiation results in good heat transmission which, in the case of films, is additionally assisted by the low film thickness.

A polymethyl methacrylate glazing material for buildings and vehicles containing an interference pigment for the screening of NIR radiation of a wave length between 800 and 1500 nm is disclosed in DE 2,544,245.

The pigment used has a blue-red colour and the light transmitted through the glazing material has a yellow-green 30 colour. When used in greenhouses, this glazing material has the disadvantage that portions of visible light which cannot be utilized by the plant are transmitted and, on the other hand, the red portion of visible light which can be utilized by the plant is screened off by said glazing material. Furthermore, the transmitted green portion has the additional 35 disadvantage that it contributes to heating of the greenhouse by virtue of its conversion into long wave light.

EP-A 0,428,937 describes a grey-white coating composition for greenhouses consisting of a polymer substrate and

reflecting particles suspended therein. These particles are aluminium platelets or mica platelets coated with titanium dioxide. The coating composition is used for temporary coatings in extreme weather conditions (summer). In winter, it 5 can again be removed by washing it off with a water jet. More details regarding the pigment used are not given.

The coating composition has the disadvantage that not only the IR beams but also a substantial portion of the visible light which can be utilized by the plant are reflected 10 by the metal particles. The green portion of the transmitted light cannot be utilized by the plant and contributes to heating of the greenhouse.

EP-A-03 98 243 describes polymeric mulch sheets and mulch films for use in agriculture which have a green absorption colour and contain a UV stabilizer. The green sheets and films absorb a large part of the solar radiation which promotes photosynthesis and plant development (PAR), and transmits enough solar radiation so as to heat the soil beneath such films and sheets. Such mulch films and sheets reduce 20 weed growth but they have the disadvantage that the photosynthetically active radiation is absorbed and is lost for the useful plant.

L.M. Mortensen and E. Stromme describe in *Scientia Horticulturae* 33 (1987), 27-36 the effects of light quality 25 on some greenhouse crops. Different light qualities were established in growth chambers placed outdoors by selective screening of the natural light spectrum in the chambers. The PAR level was the same at all light qualities. Blue light containing a high red/far-red ratio reduced the dry weight 30 compared to natural (N), green, yellow and red light in chrysanthemum, tomato and lettuce. Plant height in chrysanthemum and tomato was strongly reduced by blue compared to N light, and strongly increased by green and yellow light.

The aim of the invention is to provide a composite 35 material for the screening of intensive irradiation by sunlight, which material reflects, apart from the IR portion, also a green portion of visible light which cannot be utilized by the plant.

A further aim of the invention is to provide a composite material useful as mulch film or mulch sheet which do not absorb the photosynthetically active radiation.

Lastly, it is the aim of the invention to provide a composite material useful as covering material for the influencing of plant morphogenesis.

This object is achieved according to the invention by a composite material comprising a polymer and an additive and the customary stabilizers and processing aids necessary for 10 the particular polymer.

The additive according to the invention is a platelet-shaped material or a platelet-shaped material coated with one or more metal oxides.

Usually the platelet-shaped material consists of layered silicate, synthetic mica, glass platelets, ceramic platelets and silicia platelets.

Preferably the layered silicate is mica, pyrophyllite, sericite, talc or kaolin.

The platelet-shaped material coated with one or more 20 metal oxides is preferably an interference pigment.

The preferably used interference pigments are platelet-like pigments consisting of platelet-like substrate, such as for example, mica, kaoline or talc, and one or more metal oxide films thereon.

25 The metal oxides which can be used are only those oxides which allow the preparation of interference pigments, for example, oxides of the metals tin, titanium, zirconium, chromium, cerium, iron or tungsten.

In order to be able to produce interference colours, 30 a certain film thickness is necessary. This film thickness depends on the metal oxide used. If titanium dioxide is used, it is for example advantageous to apply a film in a thickness of 120 to 160 nm for obtaining a pigment having a green interference colour.

35 In the invention the substrate preferably has a diameter of from 1 to 200  $\mu\text{m}$ , and more preferably from 5 to 60  $\mu\text{m}$  and a thickness of from 0,1 to 10  $\mu\text{m}$ , preferably from 0,5 to 1,5  $\mu\text{m}$ .

The additive content of the composite material is 0,1 to 30% by weight, preferably 0,5 to 5% by weight, based on the polymer. The additive content depends on the film thickness of the composite material. The term "additive" includes 5 also mixtures of additives.

For the composite materials according to the invention, it is possible to use as additive commercially available interference pigments, which are available under the trade name Iridin<sup>R</sup> manufactured by E.MERCK, Darmstadt. They 10 consist of mica, TiO<sub>2</sub> and SnO<sub>2</sub>.

The polymer according to the invention may be an organic or inorganic polymer.

Said organic polymers used for the preparation of the composite materials are transparent materials like polyolefins, co- or terpolymers, for example low-density polyethylene (LDPE), vinyl ester copolymers like ethylene-vinyl acetate copolymer (EVA), fluoropolymers, co- or terpolymers like polytetrafluoroethylene (PTFE) and polyvinylidene chloride (PVDC), polyvinyl chloride (PVC), polycarbonate (PC), polymethylacrylate (PMMA) or mixtures of transparent polymers. The 20 term "polymer" may include mixtures of polymers.

As inorganic polymer glass may be used.

The composite materials additionally may contain the stabilizers and processing aids necessary for the particular 25 polymer.

The composite material according to the invention can be used in the form of films, sheets, spinbonded and woven fabrics and profiles, preferably in plant cultivation and in plant growing (agriculture and gardening). The composite 30 material according to the present invention can be used, for example, in the form of films or plates for greenhouses, as tunnel films and mulch films. Furthermore, it can be used in the form of film for covering of soils or as substrate film. It can be produced using the customary plastic processes, 35 such as film blowing, film casting, coextrusion, cast film extrusion or lamination in the form of films, multilayer films or sheets.

For optimum effect of the interference pigment, it is necessary to align the pigment platelets in the composite

material parallel to the surface and parallel to one another. This must be taken into account, for example, in casting. In other processing procedures, this parallel alignment necessarily follows from the flow characteristic of the melt.

5 For the effectiveness of the pigment, it is immaterial whether the polymer is completely coloured or the pigment is present in one or more layers of a multilayer system. Such multilayer systems can be produced by coextrusion, coating, extrusion coating, laminating or printing.

10 The composite material according to the invention used as covering for greenhouses preferably contains a green interference pigment. That means that the longwave infrared radiation is absorbed, the near infrared radiation is reflected together with the green portion of the incoming visible 15 light and only the red and blue portions of visible light which can be utilized by the plant are transmitted and scattered.

On the other hand the composite material absorbs the infrared radiation which is reflected or emitted by the 20 ground or the contents of the enclosed areas and prevents a too strong cooling of the enclosed areas at night. Consequently, the incoming light is used optimally for the climate under the composite material.

In case the composite material according to the invention is used as mulch film or mulch sheet it is desired to screen the photosynthetically active radiation in order to prevent the growth of weeds. Therefore, according to the invention an additive, preferably an interference pigment is used, which reflects the PAR. The reflection of the PAR by 30 the mulch film or sheet has the advantage that the useful plant which grows above the mulch film can use the reflected PAR for its growth. In case of a black film or a green film coloured with an absorption pigment the PAR is absorbed and is lost for the useful plant.

35 According to the invention a red-blue interference pigment, for example IRIODIN<sup>R</sup> 219 Rutile Lilac Pearl, is used. This mulch film or mulch sheet can be used alone or in combination with a second layer or a separate film containing known absorption pigments below. This could be done, for ex-

ample, in a two or multilayer film in which the interference pigment is in the upper layer while the absorption pigment is in the lower layer.

As a result the mulch films or mulch sheets according 5 to the invention improve the microclimate below the film (temperature and humidity of the soil) and in addition to known films improve the growth of the useful plants by reflecting the PAR.

When the composite material according to the invention 10 is used for modifying the plant morphogenesis an additive, preferably an interference pigment is used which changes the spectral distribution of the sunlight.

For certain crops growers want to modify the plant 15 morphogenesis. Morphogenesis is the influence from environmental factors on the shape and appearance of the plant.

It is well known in agriculture that growth, blooming and crops can be influenced by the spectral composition of light.

Plants contain pigments which can deduct of the incoming 20 light, certain wave lengths and their intensity. The most important plant pigments for morphogenesis are the phytochrome and cryptochrome. Phytochrome absorbs mainly in the Red/Far Red region (680 nm/730 nm). Cryptochrome absorbs in the blue and UV-A region (315 to 500 nm).

25 Photoselective light in the Blue or in the Red/Far Red region activates the plant pigments positively or negatively and plays an important role in growth and flowering, for example.

These relations were found by agricultural experiments - in which different lamps, filters and coloured films 30 were used. The use of filters and coloured films always has the disadvantage of a loss of energy which reduces the efficiency.

The present invention describes a novel method to 35 influence the photogenesis by using interference pigments. Light passing through the composite material containing interference pigments can influence the physiological responses of plants. This is due to changes in the Red/Far Red ratio, Blue/ Red ratio and Blue/Far Red ratio which control plant

morphology. Reducing Red/Far Red ratio with a blue interference pigment like Iriodin<sup>R</sup> 225 Rutile Blue Pearl or Iriodin<sup>R</sup> 221 Rutile Fine Blue results in plants with longer internodia, fewer branches and longer but smaller leaves.

5         Bolting can be reduced by increasing the Blue/Red ratio (relatively richer in Blue than in Red) using a composite material which contains a yellow interference pigment like Iriodin<sup>R</sup> 205 Rutile Platinum Gold.

When a more compact plant growth (suppressed stem 10 elongation) is required a high Red/Far Red ratio combined with a high Blue/Red ratio is obtained by a composite material containing a yellow-green interference pigment of second order. In these cases the use of hormonal growth regulators could be avoided.

15         Depending on the plants and the aim, a suitable interference colour can be chosen of the wide range of colours. The maximum reflection (minimum transmission) can be brought to every wave length by creating a layer thickness of the interference pigments. The selection has to be done according 20 to the state of the knowledge. The use of interference pigments gives the possibility to select a certain spectrum without the loss of too much radiation energy.

As a consequence of the transparency and the absence 25 of absorption in the interference pigments used, the incoming light is hardly diminished by scattering and absorption.

Measurements have shown that only about 5% of the increasing light is absorbed. The low heat conductivity of the pigment used has a positive effect on the thermal resistance and the heat storing capacity of the composite materials according to 30 the invention. The selective reflection results in a uniform climate within the greenhouse in almost any weather without screening off, to any great extent, the portions of visible light which can be utilized by the plant.

35         Example 1

0,5% of dioctyl phthalate is added as adhesive to high-density polyethylene granules (extrusion type suitable for film production, MFI4), followed by mixing in a tumbler mixer until the surface of the granules has been homogeneous-

ly wetted. After addition of 1% of Iriodin<sup>R</sup> 235 Rutile Green Pearl (a green TiO<sub>2</sub>/mica interference pigment) mixing is continued for a short period, as a result of which the pigment platelets form a uniform strongly adhering film on the 5 granules.

This colour compound thus prepared is formed into a film of 200 µm in thickness by means of a film blowing extruder. Viewed by reflected light, the film shows a strong green interference colour, while when viewed by transmitted light a 10 bluish red colour is visible.

#### Example 2

The film production takes place analogously to Example 1. However, for colouring the pigment was predis-15 persed in a high percentage colour master batch (for example 40% of pigment) prior to production. Furthermore, Iriodin<sup>R</sup> 9235 Rutile Green Pears WR is used instead of Iriodin<sup>R</sup> 235. The addition of 2.5% of the master batch also gives a film having a pigment content of 1%.

20

#### Example 3

Five parts by weight of epoxidized soya bean oil, 3 parts by weight of an organotin stabilizer, 1 part by weight of lubricant and 0.5 part by weight of a benzotriazole UV ab-25 sorber are added to 100 parts by weight of PVC suspension, and 0.2 part by weight of a green third order TiO<sub>2</sub>/mica interference pigment is added in a high-speed mixer, and the mixture is cooled to below 50°C by means of water cooling at low motor speed.

30 This pigmented dry blend is then formed into a double-walled sheet via a twin screw extruder using the appropriate profile tool. When viewed by reflected light, the sheets show a strong green interference colour and, when viewed by transmitted light a diffused, uniform, bluish red.

35 The recorded reflection and transmission spectra show that in the products obtained a high percentage of the NIR and the green light is reflected. The wave length distribution of the transmitted light is in a range favourable for

plant growth. Absorption within visible light and within the NIR is below 5%.

Example 4

5        10% of Iriodin<sup>R</sup> 231 Rutile Fine Green are thoroughly dispersed in a commercially available, transparent gravure printing ink suitable for printing PVC by means of a propeller stirrer, and that dispersion is printed on a transparent PVC film by means of the gravure printing process. To prevent 10 the pigment platelets, whose diameter can be up to about 25  $\mu\text{m}$  from being destroyed, the screen size selected for the pigment chosen is 70 lines/cm. At an etching depth of the colour cups of about 40  $\mu\text{m}$ , a printed film of 30  $\mu\text{m}$  in thickness which, after drying, forms a film of about 10  $\mu\text{m}$  in 15 thickness is obtained.

This gives a thin radiation-screening film which, for example, can be applied to glass surfaces by means of an adhesive film.

20        Example 5

A LDPE film with a thickness of 50  $\mu\text{m}$  is produced by film blowing of a mixture of 6 parts of master batch containing 30% by weight Iriodin<sup>R</sup> 219 Rutile Lilac Pearl and 94 parts of LDPE.

25        The film looks green in transmitted light and lilac in reflection. The film is used as mulch film.

Example 6

A LDPE film with a thickness of 50  $\mu\text{m}$  is produced by 30 film blowing of a mixture of 6 parts of a masterbatch containing 30% by weight of Iriodin<sup>R</sup> 205 Rutile Platinum Gold and 94 parts of LDPE.

The film looks blue in transmitted light and yellow in reflection. The film is used for covering of plants in order 35 to influence the plant morphogenesis.

CLAIMS

1. Composite material for the selective screening of  
5 radiation, comprising a polymer, an additive and the customary stabilizers and processing aids necessary for the particular polymer.
2. Composite material according to claim 1, characterized in that the additive is a mica or a platelet-shaped  
10 material coated with one or more metal oxides.
3. Composite material according to claim 2, characterized in that the platelet-shaped material consists of layered silicates, synthetic mica, glass platelets, ceramic platelets and silica platelets.  
15
4. Composite material according to claim 3, characterized in that the layered silicate is mica, pyrophyllite, sericite, talc or kaolin.
5. Composite material according to claim 2, characterized in that the platelet-shaped material coated with one  
20 or more metal oxides is an interference pigment.
6. Composite material according to one of the claims 1 to 5, characterized in that the polymer is an organic or inorganic polymer.
7. Composite material according to claim 6, characterized in that the organic polymer is a low-density polyethylene, ethylene-vinylacetate copolymer, polytetrafluoroethylene, polyvinylidene-chloride, polyvinyl chloride, polycarbonate, polymethacrylate or mixtures thereof.  
25
8. Composite material according to claim 6, characterized in that the inorganic polymer is glass.  
30
9. Composite material according to claims 1 to 8, characterized in that it contains 0,1 to 30% by weight, preferably 0,5 to 5,0% by weight, of the additive based on the polymer.  
35
10. Greenhouse containing composite materials according to claims 1 to 9.
11. Use of the composite material according to claims 1 to 9 for plant growing and plant cultivation.

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<b>(22) International Filing Date:</b> 31 August 1993 (31.08.93)		<b>(81) Designated States:</b> AU, BR, CA, FI, HU, JP, KR, NZ, RU, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
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**(54) Title:** COMPOSITE MATERIAL FOR THE SCREENING OF RADIATION**(57) Abstract**

Composite material for the screening of radiation, comprising a polymer, an additive and the customary stabilizers and processing aids necessary for the particular polymer. The additive is preferably an interference pigment.

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A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 5 C08K11/00 C08K9/02 A01G9/22 C03C14/00

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B. FIELDS SEARCHED

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 428 937 (STATE OF ISRAEL MINISTRY OF DEFENCE ARMAMENT DEVELOPMENT AUTHORITY) 29 May 1991 cited in the application see example 1 see claims 1-4,6-8 ---	1-6,9-11
X	DE,A,25 44 245 (RÖHM GMBH) 14 April 1977 cited in the application see page 8; example 1 see claim ---	1-6,9
X	EP,A,0 340 313 (NIPPON STEEL CHEMICAL CO) 8 November 1989 see page 25; example 6; table 1 ---	1-6,9 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

Date of mailing of the international search report

8 April 1994

27.04.94

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Character of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,16 94 349 (W.R. GRACE & CO.) 5 November 1970 see examples see claims 1-3 ---	1,6,7
X	EP,A,0 193 902 (PHILLIPS PETROLEUM COMPANY) 10 September 1986 see claims 1,3,5 ---	1,6,7
X	DE,A,41 34 839 (MINNESOTA MINING & MANUFACTURING) 30 April 1992 see examples 4-5 see claims 1-3,5-8 ---	1-3,6,9
X	DE,A,29 40 230 (P. HARI) 30 April 1981 see page 12, line 10 - line 31 see page 15, paragraph 3 - page 16, paragraph 1 -----	1,6,8

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/EP 93/02380

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
2.  Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3.  Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See form PCT/ISA/206 mailed on 11.01.1994

1. Claims 1-5,6 (organic polymer), 7,9-11 (organic polymer)
2. Claims 1-6 (inorganic polymer), 8,9-11 (inorganic polymer)

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

## Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 93/02380

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0428937	29-05-91	AU-A- CA-A-	6669290 2029941	23-05-91 21-05-91
DE-A-2544245	14-04-77	AT-B- CA-A- FR-A, B NL-A- US-A-	359720 1085205 2326549 7610912 4090773	25-11-80 09-09-80 29-04-77 05-04-77 23-05-78
EP-A-0340313	08-11-89	JP-A- JP-A- WO-A- US-A-	1121371 1126376 8904351 5154768	15-05-89 18-05-89 18-05-89 13-10-92
DE-A-1694349	05-11-70	FR-A- GB-A-	1546062 1136350	
EP-A-0193902	10-09-86	US-A- CA-A- JP-A- US-A- US-A- US-A-	4661299 1278676 61211351 4790965 4767799 4968726	28-04-87 08-01-91 19-09-86 13-12-88 30-08-88 06-11-90
DE-A-4134839	30-04-92	US-A- JP-A-	5232775 4266944	03-08-93 22-09-92
DE-A-2940230	30-04-81	DE-C-	2954516	09-04-87



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